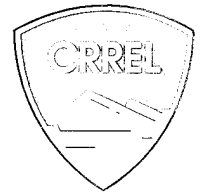


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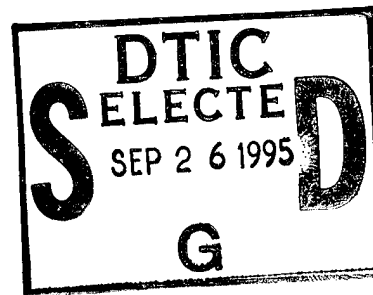
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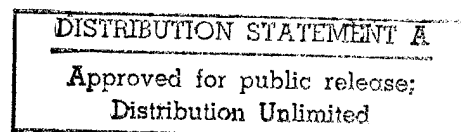
Dispersion-by-Chemical-Reaction Technology to Stabilize Asphalt Tar Eareckson Air Force Station, Shemya, Alaska

Gurdarshan S. Brar and Giles M. Marion

March 1995



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Abstract

Many military installations have soil contamination, ranging from heavy metals to petroleum products. This report evaluates the Dispersion-by-Chemical-Reaction (DCR) technology to remediate soil contaminated by asphalt tar at Eareckson Air Force Station on Shemya Island in Alaska. The DCR technology uses patented hydrophobized CaO (lime) as the primary reagent for stabilizing heavy metals and organics in a relatively insoluble CaCO₃ matrix. Field work, conducted at Shemya in January 1994, showed DCR technology to significantly affect soil physical and chemical properties: moisture significantly decreased and temperature significantly increased during the mixing step (up to 95°C). The resultant product had a relatively low specific gravity (2.08 g cm⁻³) and a coarse texture (37% gravel, 56% sand and 6% fines). Because of the coarse texture, the treated soils had high hydraulic conductivities ($>2.7 \times 10^{-4}$ cm s⁻¹). Reducing these for some applications will necessitate mixing with finer textured silts or clays. There were a few significant differences in chemical concentrations between DCR-treated and untreated soil, with the DCR-treated material generally having higher concentrations. This counterintuitive outcome is probably attributable to a poor mixing of the lime reagent and asphalt tar and the greater surface area of the treated end product. However, in all cases, contaminant levels were well below drinking water standards. In an independent laboratory-scale test on fuel-contaminated soils from Shemya, the DCR process successfully lowered organic chemical concentrations.

For conversion of SI units to non-SI units of measurement consult ASTM Standard E380-93, *Standard Practice for Use of the International System of Units*, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

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Special Report 95-11



**US Army Corps
of Engineers**

Cold Regions Research &
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PREFACE

This report was prepared by Dr. Gurdarshan S. Brar, Research Physical Scientist, and Dr. Giles M. Marion, Research Physical Scientist, Geochemical Sciences Division, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory. The research reported here was funded in part by the U.S. Air Force through MIPR N6550193N0078 and in part by the Office of the Chief of Engineers through CPAR Project AC910260, *Site Remediation via Dispersion by Chemical Reaction (DCR)*, to evaluate DCR technologies for handling different types of contaminants at DOD facilities.

The authors thank members of the SOUND Environmental Services Team (Edward Cronick, James R. Payne, Jeffrey Bauman, John Bayliss, Steven Fitzhugh) for the field implementation of the DCR process. They also thank Michael Stanka and Patricia Striebich of the U.S. Air Force for funding and overseeing the field implementation.

Technical review was provided by Edwin J. Chamberlain and Daniel Leggett, both of CRREL.

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Dispersion-by-Chemical-Reaction Technology to Stabilize Asphalt Tar

Eareckson Air Force Station, Shemya, Alaska

GURDARSHAN S. BRAR AND GILES M. MARION

INTRODUCTION

Lime-based stabilization-fixation technologies

Definitions

To understand the following discussion, it is first necessary that we define three terms. *Solidification* is a physical process that converts waste into an easily handled solid and significantly reduces hydraulic conductivity. The resulting product is a solid, impermeable matrix with high structural integrity. *Stabilization* is a process where formulated reagents combine with waste to maintain contaminants in their most immobile form (Grood 1991). The technology's goal is to reduce waste solubility or chemical reactivity through the addition of specific reagents. *Fixation* is a treatment process by which a waste material is chemically or physically changed to improve leaching characteristics and reduce damage to biological systems.

Historical development

Lime is one of the oldest chemicals used on Earth (Wray 1991). History does not record its discovery; however, lime is mentioned in the Bible and in documents from ancient China as well as Egypt, dating back about 6000 years. Lime and its by-products used in the waste treatment industry are summarized in Table 1. Many lime products and by-products behave differently from each other. Chemically, these by-products are poorly defined, and their use in place of lime requires extensive analysis to determine the equivalent quantity of lime. The most common forms of lime used in waste treatment are quicklime or unslaked lime (CaO) and hydrated or slaked lime [Ca(OH)₂]. In 1989, more than 34 billion pounds of lime were produced in the United States (Wray 1991).

Lime is often used in water treatment to precipitate potentially toxic metals and to neutralize acids (Lewis and Boynton 1976, Boynton 1980).

Table 1. Characteristics of major lime and limestone products, and by-products used in waste treatment (after Malone and May 1991).

Reagent	Formula or composition	Bulk density (kg m ⁻³)	pH
High calcium quicklime	CaO	769-1121	10.5-12.4
Dolomitic quicklime	CaO-MgO	790-1400	9.0
High calcium hydrate	Ca(OH) ₂	400-641	10.5-12.4
Normal dolomitic hydrate	Ca(OH) ₂ Mg(OH) ₂	400-560	9.0
Dolomitic pressure hydrate	Ca(OH) ₂ Mg(OH) ₂	480-640	9.0
High calcium limestone	CaCO ₃	—	6.5
Dolomitic limestone	CaCO ₃ MgCO ₃	—	—*
Lime kiln dust	10-15% lime	—	~ 12.4
Cement kiln dust	Lime varies	—	~ 12.4
Fly ash†	Lime varies	—	~ 12.4
Waste lime	Lime varies	—	~ 12.4

* Non-reactive.

† High calcium fly ash may have up to 2.4% uncombined CaO.

Using lime to precipitate metals requires pH adjustment to produce the lowest solubility. Most potentially toxic metals (e.g., cadmium, chromium, lead and nickel) are amphoteric, meaning that metal hydroxides show increased solubility at very low and high pH values. Weeter and Jones (1987) concluded that a lime-fly ash additive significantly reduced the chromium (Cr) concentration of industrial sludge that was high in copper (Cu), nickel (Ni), and Cr. The concentrations of Cu and Ni were reduced by solidification. Furthermore, they stated that a lime-fly ash admixture was more cost effective than other agents, such as Portland cement, lime or sodium silicate. On the other hand, Malone et al. (1987) found that the fly ash-lime additive produced an overall lowering of the conductivity of the leachate but did not significantly lower the losses of heavy metals. A process using soluble silicate and cement additives gave the best results for the containment of heavy metals.

Crawley et al. (1984) outlined techniques for using hydrated, high-calcium lime to treat acidic sludges. Remedial action using hydrated lime injection proved very effective in preventing groundwater pollution under and around acid waste pits. Morgan et al. (1984) developed and tested a variety of lime and by-product mixtures for treating oil refinery sludges. Blacklock et al. (1982, 1984) described a technique for injecting a lime-fly ash grout into landfills.

In 1971, EIF (Ecology of France) developed lime-based fixation technology to detoxify wastes rich in organic content (Separation and Recovery Systems, Inc. 1987). The following are examples of organic wastes treated with this technology: crude oil, refinery intermediate or final products, halogenated chemicals (e.g., PCBs), pesticides, sludges, tars, painting wastes and acid sludges. The permeability of the treated and compacted refinery impoundment sludge waste was less than $1.0 \times 10^{-12} \text{ cm s}^{-1}$.

In Dallas, Texas, Morgan et al. (1984) used several solidification agents to treat $19 \times 10^6 \text{ L}$ of 30-year-old oil refinery sludge. The best solidifying agent found was fresh and stale cement kiln dust. Furthermore, the kiln dust was also tested in combination with small amounts of sulfur, cement and lime. They observed excellent solidification with cement and lime, although sulfur did not increase the strength significantly. This on-site solidification and disposal is an example of a remedial action in which careful planning and investigation of numerous alternatives led to a suc-

cessful cleanup operation. The solidification process is simple, economical and potentially applicable to other waste-disposal sites, and waste kiln dust may be worth trying elsewhere.

Zenobia and Turco (1985) studied the lime-based stabilization technique to remediate a hazardous waste site containing basins of inorganic sludges, incineration residues and spent biomass. They found that fly ash in combination with lime and lime kiln dust were the best stabilizing agents. In France, Such and Roux (1981) treated oil spills with quicklime and hydrophobic lime.* They reported that the chemical reaction of dehydration occurred immediately in quicklime and was relatively delayed with hydrophobic lime.

Koper et al. (1993) reported that CaO is an effective solid reagent for destroying chlorocarbons (CCl_4). Furthermore, in an editorial note, Rittenhouse (1993), discussing the work of Olga Koper, Young-Xi Li and K.J. Klabunde at Kansas State University, wrote about CaO as an effective reagent for the destruction of CCl_4 .

Soundararajan (1991) found a strong interaction between high-calcium fly ash (CaO) and polychlorinated biphenyls (PCBs), resulting in the total destruction of the PCBs. Although he concluded that a catalyst was probably responsible for destroying the PCBs, the specific catalyst responsible is unknown. Einhaus et al. (1991) reported that PCB-contaminated soil treated with quicklime and water had significantly reduced (60 to 80%) PCB concentrations after 5 hours of treatment. However, they concluded that use of reactive quicklime as an in-situ treatment may be counterproductive owing to the potential for migration of PCBs as vapor or airborne particulates. Sediak et al. (1991) attributed most PCB losses to volatilization caused by the high heat of the CaO hydration reaction. They concluded that the "quicklime" treatment, per se, was not effective for PCB-contaminated soil.

Lime and lime products are useful in the engineered disposal of both nontoxic and hazardous wastes. In some cases lime can be used to convert hazardous waste to nonhazardous waste. Malone (1984) reported that lime has great potential as a neutralizing and cementing agent in waste management. Furthermore, he suggested that the application of lime in hazardous waste reduction processes should increase

* Using Professor Bolsing's RM reagent, see *DCR Technology* section.

because new ideas about its use in liners, lime-fly ash grout injection and enhancement of methane production have been evaluated and found to be safe and useful. Lime stimulates the activity of anaerobic, methane-generating bacteria responsible for the decay of refuse. Methanogenic bacteria function best in the pH ranges of 6.4 to 7.4; however, some methane producers can operate at high pHs of 9.0 (Klass 1984). Lime in the form of quicklime is also used in drying semi-solid wastes. The hydration reaction of quicklime eliminates water from the system and produces a dry product that is easy to handle.

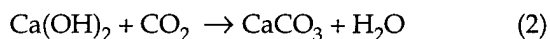
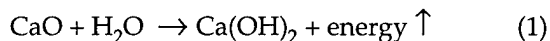
Malone and May (1991) found that the porosity and permeability of lime-amended soil were greatly reduced by precipitation of contaminants in intergranular spaces. Initially, the amended soil had a permeability of $3.5 \times 10^{-6} \text{ cm s}^{-1}$; after 20 pore volumes of an acidic waste had passed through the column, the permeability decreased to $4.0 \times 10^{-8} \text{ cm s}^{-1}$. In contrast, the permeability of the untreated soil ranged from 4.0×10^{-6} to $1.0 \times 10^{-6} \text{ cm s}^{-1}$ after contact with 24 volumes of acidic waste. Amending the soil with lime decreased the permeability, reduced the amount of leachate passing through the liner, and reduced the total dissolved solvent content, trace metal, and radio nuclide concentrations in the waste that moved through the liner. The lime-amended liner was considered to be a very successful method for reducing the discharge of pollutants from acid waste piles.

Quicklime mixed with clay soils has been used to produce hard, impervious soil liners in stock ponds, small earth dams and irrigation channels (Gutschick 1978). A compacted lime liner was constructed by BASF Corporation for a hazardous waste landfill on the Island of Flotzgrun near Speyer, Germany (BASF 1983).

DCR technology

The Dispersion-by-Chemical-Reaction (DCR) technologies are a group of patented waste treatment processes developed by Professor Friedrich Boelsing over 18 years ago in Europe for the stabilization of heavily oiled sludges, water-in-oil emulsions, oil-contaminated soil and industrial wastes such as acid-tars (Boelsing 1988, Payne et al. 1992). Hydrophobized CaO is used in the DCR process. Calcium oxide, in its pure state, is hydrophilic. Hydrophobic and oleophilic lime is prepared by treating CaO with natural fatty acids, a process that delays the hydration step and allows the fatty acid-coated CaO

reagent to preferentially adsorb oils during a mixing step. The delayed hydration then produces calcium hydroxide $[\text{Ca}(\text{OH})_2]$, which is fractured into submicron-sized particles (eq 1). This hydration reaction is highly exothermic. Hydrate particles are homogeneously charged throughout their internal and external cavities with the oil phase. The finely dispersed $\text{Ca}(\text{OH})_2$ then slowly reacts with natural CO_2 to generate relatively insoluble CaCO_3 (eq 2).



Thus, the oil components are immobilized in a CaCO_3 matrix to levels passing U.S. Environmental Protection Agency's Toxic Characteristic Leaching Procedure (TCLP) requirements. Other physical properties of the DCR product that facilitate lower chemical leaching are the compactibility of the soil-like product, which lowers the hydraulic conductivity, and the hydrophobicity of the product, which resists absorption of water. During the initial mixing step, other reagents can be added for specific reactions. For example, a hydrophobized nucleophilic reagent has been used for dehalogenation of PCBs (Payne et al. 1992).

Site background

Shemya Island ($5.6 \times 2.4 \text{ km}$) is located at the western tip of the Aleutian Archipelago, 2400 km southwest of Anchorage (Fig. 1). Historically, Shemya has been uninhabited (CH2M Hill 1990). The earliest written records of human activity were by Russians who planted blue foxes on Shemya for fur farming in 1775. In 1943, the U.S. Army's 4th Infantry and 18th Engineering Regiments developed Shemya and constructed a runway and aircraft hangars for use in the war against Japanese forces then occupying the nearby islands of Attu, Agattu and Kiska. Today, the U.S. Air Force occupies the entire island (Fig. 1).

The primary mission of the Eareckson Air Force Station is to monitor space and missile activities. About 400 Air Force personnel are stationed there to operate and maintain all structures, utilities and exterior facilities, and to provide base support, with an additional civilian work force of 300.

Shemya Island is dominated by a persistent low pressure system known as the Aleutian Low. Frequent storms track across the north Pa-

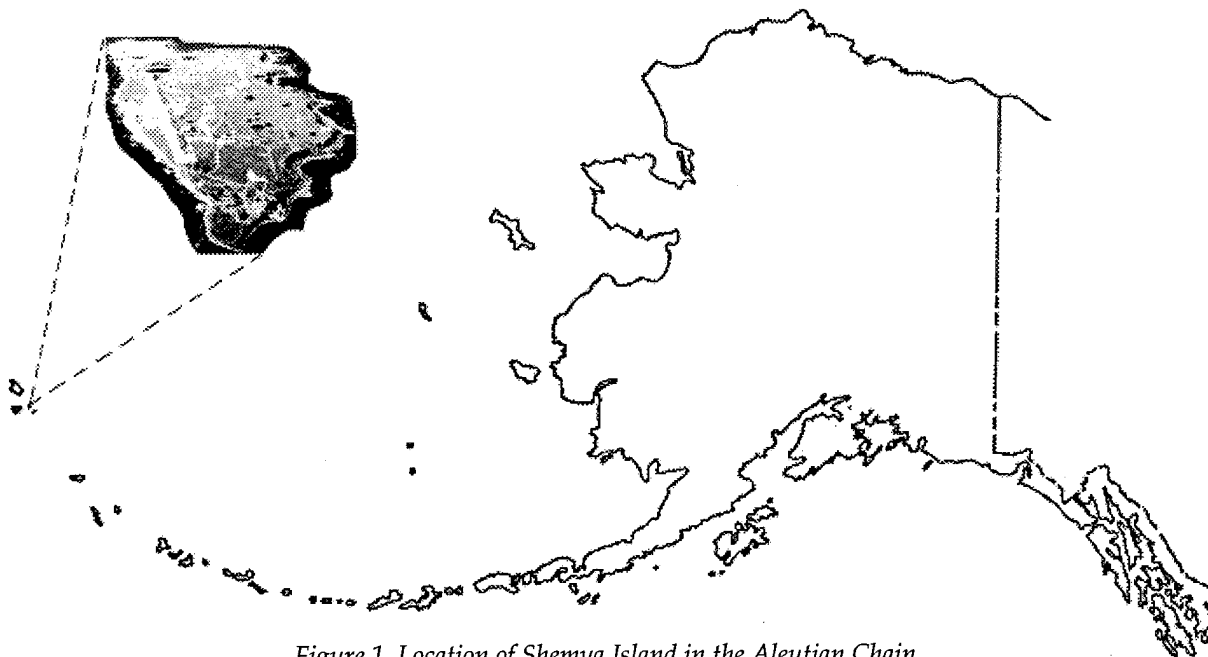


Figure 1. Location of Shemya Island in the Aleutian Chain.

cific into the Aleutian Islands. The Aleutian low pressure cells are responsible for the relatively mild maritime climate of the Aleutian Islands. Summer fogs are severe and preclude any flying as often as one day in four. The persistent wind, fog and salt spray cause highly corrosive and harsh conditions.

The mean annual temperature is 3.6°C. The minimum and maximum recorded temperatures are -13.9 and 17.2°C, respectively; however, the diurnal temperature variation rarely exceeds 6°C. Measurable winds are recorded 363 days yr⁻¹, with a mean annual wind velocity of 32 km hr⁻¹. Wind direction is evenly distributed without any true prevailing wind direction. Precipitation falls more than 330 days yr⁻¹, with the annual average being 79.5 cm. The maximum 24-hour rainfall was 13.2 cm during October 1962. The average annual snow fall is 178 cm. Drifting snow and driving rain are common in winter because of strong wind velocities.

Eareckson AFS has several types of soil contamination problems that are the result of historical and ongoing Air Force operations. The work contained in this report is focused on a site identified as PS-9 Asphalt Tar Drum Storage Area. The site was contaminated as a result of leaked asphalt tar stored in 55-gal. drums.

Objectives

The major objectives of this project at Eareckson AFS are to:

1. Gather data on the physical and chemical properties of the DCR-treated asphalt tar material.
2. Evaluate the ability of DCR technology to stabilize asphalt tar contaminated soil in cold regions.

EXPERIMENTAL PROCEDURES

DCR transportable treatment unit

SOUND Environmental Services, Anchorage, Alaska, under Contract No. DACA39-93-C-0147 with CRREL, demonstrated the DCR technology at Eareckson AFS, Shemya. To treat the asphalt tar waste, SOUND used a skid-mounted Transportable Treatment Unit (TTU, Fig. 2). The TTU consists of a mixer, a weigh batch hopper and conveyer assemblies. Asphalt tar was excavated with a Link-Belt excavator and stockpiled on the site (Fig. 3). Large frozen chunks of waste material (mixture of tar-soil-gravel) weighing approximately 2 to 5 kg were observed.

An enclosed lime feed system (Fig. 4) was tried by SOUND to minimize the effect of wind on the finely powdered lime. However, this previously untested system failed because the finely textured lime blew out of every small orifice and because of the steep angle to the weigh batch hopper. Next, SOUND started feeding lime directly into the weigh batch hopper with the help of the Link-Belt excavator (Fig. 5). This technique polluted the air with lime and was unsafe

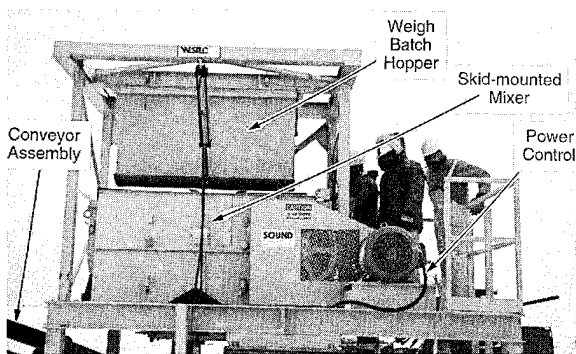


Figure 2. Transportable treatment unit.



Figure 3. Stockpiled excavated asphalt tar material showing large frozen chunks of the material.



Figure 4. SOUND personnel assembling enclosed lime feed system.



Figure 5. Direct lime feed into the weigh batch hopper.

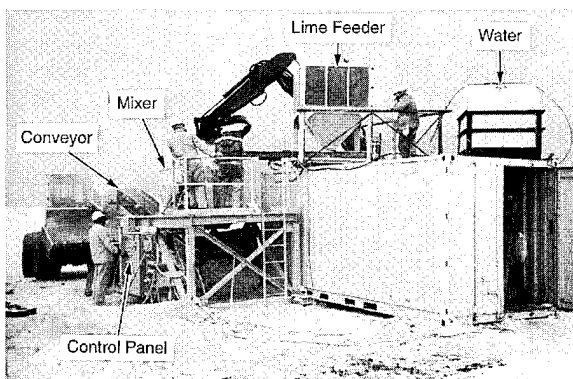


Figure 6. Lime feed hopper placed on top of the metal storage van.



Figure 7. Inspecting DCR-treated soil-like material.

for the workers. Then, the hydraulic system controlling the weigh batch hopper failed. Finally, SOUND removed the weigh batch hopper and installed the lime feed hopper on top of a metal van used for storage of tools and equipment (Fig. 6). This was the system used to treat the asphalt tar.

The excavated asphalt tar material was added to the pug-mill mixer and lime was metered in on the basis of the volume of tar added. Occasionally, water was also added to the mixture at the discretion of the mixing overseer. The chunky waste material was converted into a soil-like material (Fig. 7). However, some small tar balls (0.5

kg) were still found in the treated material. The detailed on-site operation of the DCR TTU is further described in Payne et al. (1994).

Physical analyses

Soil water content and temperatures were determined at the DCR treatment site in Shemya, Alaska. Two bulk soil samples (18 kg each) for laboratory physical tests were collected by mixing different batches of DCR-treated asphalt material in the field. These samples were air-freighted to CRREL without any special provisions for preservation.

Three soil samples were used in the CRREL physical tests. Samples 1 and 2 were from the two separate buckets, and sample 3 was a composite sample from the two buckets.

Particle size analysis

The particle sizes of the three DCR-treated soil samples were analyzed by the Soils Laboratory staff of CRREL following ASTM Standard Test Method D 422-63 (ASTM 1992). This test measured the distribution of particle sizes in the DCR-treated asphalt tar soil by sieving and sedimentation techniques. Particles larger than 75 mm (retained on No. 200 sieve) and smaller than 75 mm were separated by sieving and sedimentation (hydrometer) respectively. The soil samples were prepared as per ASTM Practice D 421 (ASTM 1992). Sodium hexametaphosphate was used as a dispersing agent. Specific gravity was determined as per ASTM Method D 854 (ASTM 1992).

Soil moisture-density relationship

The laboratory compaction characteristics of the soil were determined by using the standard effort (595 kJ m^{-3}) on the three DCR-treated asphalt tar soil samples as per ASTM Method D 698 (ASTM 1992). Tests were conducted in the Soils Laboratory of CRREL to determine the relationship between water content and dry unit weight of the soil samples, which were compacted in a 15-cm-diameter mold with a 2.5-kg rammer. The soil was placed at a selected water content in three layers into a mold, with each layer compacted by 56 blows of a rammer dropped from a distance of 30 cm, bringing the soil to a total compaction of about 595 kJ m^{-3} . The resulting dry unit weight was determined. The procedure was repeated for a sufficient number of water content values to establish a relationship between the dry unit weight and the water content of the soil. The plotted data fall into a curvilinear

relationship known as the compaction curve. The compaction curve provides the maximum water content and dry density.

Hydraulic conductivity of saturated porous materials

ASTM Standard Test Method D 5084-90 (ASTM 1992) was used to determine the saturated hydraulic conductivity (permeability) of DCR-treated asphalt tar materials with a flexible wall permeameter. The test measures one-dimensional laminar flow of water within saturated porous materials. The hydraulic conductivity of porous materials generally decreases with an increasing amounts of air in the pores. The test was done on the water-saturated DCR-treated asphalt tar materials, which were porous and contained no air. The test method assumed that Darcy's law is valid and that the hydraulic conductivity is unaffected by hydraulic gradient.

Rocks greater than 1.0 cm in diameter were excluded from the test samples, and the minimum sample size was 25 mm in diameter and 25 mm high. Soil samples were brought to the proper water content and left for stabilization. Test samples were then compacted in layers in a split mold on top of a porous plate by using a "Harvard" hammer, and the surface of each previously compacted layer was lightly scarified (roughened) with a fork. After compaction, samples were removed from the mold and height, diameter, mass and water content were measured and recorded. The dry unit weight, density and initial degree of saturation were then calculated.

A latex membrane (0.3 mm thick) was placed on the prepared test samples to isolate the water in the cell from the fluid in the test sample. The cell pressure and the pressure in the pore fluid in the test sample were initially set at 21 and 0 kPa respectively. The controls on the pressure panel were then set to link the cell and sample pressures so as to maintain a constant effective pressure difference of 21 kPa for all of the sample pressure settings. The sample pressure was then raised to 207 kPa and water was allowed to flow through the sample under a small gradient to saturate it. Four sets of hydraulic conductivity measurements were made on each sample, according to ASTM Standard D 5084 (ASTM 1992).

Freeze-thaw hydraulic conductivity tests

The procedures described in the previous section were followed to determine the hydraulic conductivity of the samples before and after one freeze-thaw cycle. The same compacted soil sam-

ples used to determine the unfrozen hydraulic conductivity were placed in a coldroom with one cold plate at the bottom and another at the top, surrounded by vermiculite insulation. Temperatures of the test samples were kept at 3°C for one night. Then the bottom and top of the sample, respectively, were maintained at 0 and -6.1°C for the next 18 hours, and at 0 and -10°C for 5 more hours. The temperatures at the bottom and top of the sample were further lowered to -3 and -12°C, respectively, for an additional 24 hours.

For thawing, temperatures were increased to 3 and 4°C at the bottom and top of the cell for 24 hours. The hydraulic conductivity tests were then performed using ASTM Method D 5084.

Laboratory determination of soil water content

ASTM Method D 2216-90 (ASTM 1992) was used to determine the gravimetric water content of DCR-treated asphalt tar samples in an on-site laboratory set up by SOUND. Samples were collected from DCR-treated batches prepared during SOUND's laboratory and field trials. Replicate samples were taken from three laboratory batches. Three soil samples were drawn from the untreated asphalt tar material for comparison. In the field, replicate samples were drawn from four different batches of DCR-treated asphalt tar material.

Fresh sample weights were recorded immediately after collection. The samples were then dried in an oven at 105°C and the dry mass of the sample and container was recorded after 24 hours. The water content was calculated as the ratio of the mass of water to the solid mass of the dry specimen.

Soil temperature

Temperatures of the DCR-treated asphalt tar material were measured in the field with copper-constantan thermocouples that were fabricated and tested at CRREL. Four thermocouples, each at 30 cm apart, were attached to a wooden stick. Two wooden sticks (eight thermocouples) were embedded horizontally into an untreated asphalt tar pile. The other two wooden sticks (eight thermocouples) were inserted horizontally into several DCR-treated asphalt tar batches. Air temperatures were measured at a 2-m height above the ground with unshaded thermocouples. Data were logged every minute with a data logger (Model CR-10, Campbell Scientific, Inc., Logan, Utah).

Chemical analyses

Soil samples for chemical analyses were collected in QC (quality certified) glass jars and stored outdoors (-5 to -1°C) until ready for shipment. Five untreated samples were collected around the excavated tar pile on 27 January 1994. Five treated samples were collected during the DCR operation on 27-28 January 1994. These chemical samples were air-freighted on "blue ice" in igloo coolers from Shemya to Anchorage on 28 January, stored in a freezer overnight, then shipped on 29 January via Federal Express to the U.S. Army Corps of Engineers Environmental Lab in Hubbardston, Massachusetts, where they arrived on 31 January.

Samples were analyzed for Total Petroleum Hydrocarbons (TPH) using EPA Methods 3550/8015M (USEPA 1992). Toxic Characteristic Leaching Procedure (TCLP) extracts for TPH were done using EPA Methods 1311/8015M (USEPA 1992). Volatile organics were determined using EPA Method 8260 (USEPA 1992). TCLP extracts for volatile organics were done using EPA Methods 1311/8260 (USEPA 1992).

Statistical analyses

The untreated (control) and DCR-treated asphalt tar samples were statistically analyzed using the SuperANOVA (Gagnon et al. 1989) and CoStat (CoHort Software 1986) software packages for chemical and physical analyses respectively. Chemical analyses that were below the level of detection were assigned values of one-half of the detection limit in these statistical tests (Clarke and Brandon 1994). The 5% significance level of a Type I error was used as the criterion in testing for significant differences between untreated and treated samples.

RESULTS AND DISCUSSION

Physical analyses

Particle size analyses

Particle sizes, coefficient of uniformity and coefficient of curvature data for DCR-treated asphalt tar material are given in Table 2. The treated material contained 37% gravel, 56% sand and 6% fine fractions and is classified as well-graded sand with silt (SW-SM) as per ASTM Standard Method D 2487 (ASTM 1992). According to soil classification standards, the SW-SM soil must contain more than 50% in the coarse fraction passing sieve no. 4 (5 mm), a finer fraction between 5 and 12%, and have a coefficient of uni-

formity (C_u) greater than 6 and a coefficient of curvature (C_c) less than 3.

The C_u is the ratio of $(D_{30})^2/(D_{10} \times D_{60})$, where D_{60} , D_{30} , and D_{10} are the particle diameters corresponding to the 60, 30, and 10% finer fractions on the cumulative particle-size distribution curve (e.g., Fig. 8). The C_u varied between 20.9 and 32.8 among the three samples. The C_c is the ratio of D_{60}/D_{10} , where D_{60} and D_{10} are the particle diameters corresponding to the 60 and 10% finer fractions on the cumulative particle-size distribution curve. The C_c was between 0.5 and 0.7 among the three samples.

Soil moisture–density relationship

Maximum moisture content and dry density of the DCR-treated material were determined from compaction curves as per ASTM Method D 698 (ASTM 1992) (Table 3). The moisture content and dry density values for samples 1 and 2 fall within the 100% saturation curve (Fig. 9); however, the water content and dry density values of sample 3 were slightly outside of it.

The specific gravity is used to calculate points for plotting the 100% saturation curve or zero air

Table 2. Particle size distribution, coefficient of uniformity and coefficient of curvature of the DCR-treated asphalt tar material.

Property	Particle diameter (mm)	Particle mass (%)			
		Sample number			Mean
		1	2	3	
Fines	< 0.08	6.2	5.7	7.0	6.3
Fine sand	0.08–0.50	17.3	15.9	16.0	16.4
Medium sand	0.50–2.00	27.4	26.3	21.3	25.0
Coarse sand	2.00–5.00	15.0	14.9	14.7	14.9
Fine gravel	5.00–19.0	27.7	30.3	33.5	30.5
Coarse gravel	19.0–75.0	6.4	6.9	7.5	6.9
Coeff. of uniformity (C_u)		20.9	23.5	32.8	25.7
Coeff. of curvature (C_c)		0.7	0.7	0.5	0.6
% passing no. 4 sieve		65.9	62.8	59.0	62.6

Table 3. Maximum soil moisture, dry density and specific gravity of the DCR-treated asphalt tar.

Sample no.	Moisture (%)	Dry density (g cm^{-3})	Specific gravity (g cm^{-3})
1	13.8	1.60	2.06
2	13.7	1.58	2.10
3	17.0	1.53	2.07
Mean	14.8	1.57	2.08

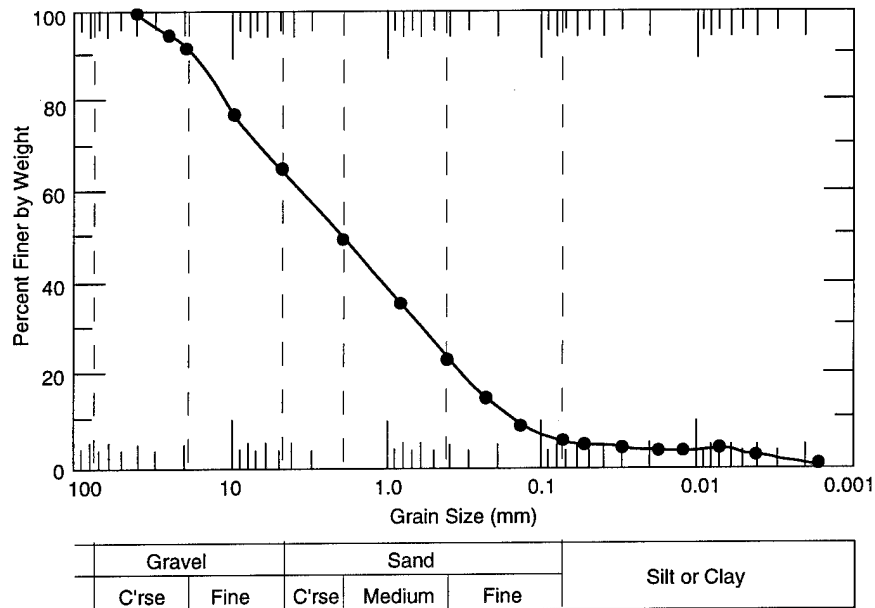


Figure 8. Soil particle size distribution for sample 1.

voids curve as per ASTM Method D 698 (ASTM 1992). Specific gravity tests were performed on the DCR-treated material passing sieve no. 4 (5 mm). The mean specific gravity of the DCR-treated sample is 2.08 g cm^{-3} compared to 2.63 and 2.66 g cm^{-3} for diesel-contaminated and

clean soil samples, respectively (G.S. Brar, unpublished data, 1992). The specific gravity of typical mineral soil is around 2.65 g cm^{-3} . The low specific gravity of the DCR-treated soil is probably attributable to the high asphalt content of the soil.

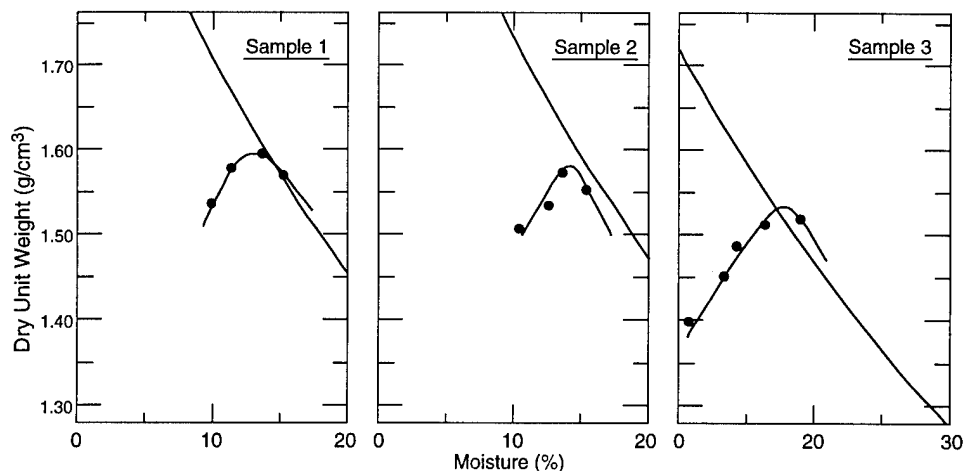


Figure 9. Relationship of dry unit weight and moisture for the DCR-treated samples.

Hydraulic conductivity of saturated porous materials

The hydraulic conductivity of the three DCR-treated asphalt tar samples ranged between 6.16×10^{-4} and 8.36×10^{-4} cm s⁻¹ at a 21-kPa back pressure (Table 4). The hydraulic conductivity decreased slightly when the effective pressure was increased to 41 kPa; however, the difference was not significant.

Rocks greater than 1.0 cm were excluded from these samples. The dry density of the compacted samples varied between 1.30 and 1.38 g cm⁻³, which are 14 to 16% lower than the target density values. The water content of the samples was 8 to 11% higher than the target water content.

Hydraulic conductivity tests were repeated by including all the rocks present in the original sample received from the field. The differences in mean hydraulic conductivities of DCR-treated samples, including or excluding rocks, are statistically not significant.

The high hydraulic conductivities may be the result of the small amounts (6.3%) of fine particles in the material, which is classified as a well-graded sand with very little silt. The hydraulic conductivity might be lowered to the regulatory limit of 1×10^{-5} cm s⁻¹ by adding clay. The other reason for high hydraulic conductivity may be the small chunks of asphalt tar still present in the treated material (Fig. 7). This situation could be avoided by heating the asphalt tar before mixing it with lime, which would lead to better mixing and a finer-textured product.

Freeze-thaw hydraulic conductivity tests

The hydraulic conductivity was determined on three DCR-treated asphalt tar samples subjected to a single freeze-thaw cycle. Although the hy-

Table 4. Hydraulic conductivity of DCR-treated material at different effective stresses and dry densities.

Sample no.	Effective stress (kPa)	Dry density (g cm ⁻³)	Hydraulic conductivity (cm s ⁻¹)	Mean hydraulic conductivity (cm s ⁻¹)
1	23	1.38	8.36×10^{-4}	7.22×10^{-4} a*
2	21	1.30	6.16×10^{-4}	
3	21	1.36	7.13×10^{-4}	
2	41	1.30	6.09×10^{-4}	6.09×10^{-4} a
Repeat samples				
1	17	1.51	8.2×10^{-4}	3.92×10^{-4} a
2	17	1.39	7.87×10^{-5}	
3	18	1.51	2.66×10^{-4}	

* Least square difference at $P < 0.05$ according to Student-Newman-Keuls test = 4.65×10^{-4} .

draulic conductivity increased with a single freeze-thaw cycle, the difference was not significant (Table 5). Chamberlain (1994) reported that freeze-thaw cycles are the major problem in cold regions affecting the design and performance of landfill containment structures and surface impoundment systems. Furthermore, he stated that the hydraulic conductivity of most

Table 5. Changes in hydraulic conductivity after one freeze-thaw cycle.

Sample no.	Dry density (g cm ⁻³)	Hydraulic conductivity (cm s ⁻¹)		
		Freeze-thaw cycles		Ratio
		0	1	
1	1.41	1.03×10^{-3}	1.12×10^{-3}	1.09
2	1.36	5.76×10^{-4}	9.85×10^{-4}	1.71
3	1.37	2.06×10^{-4}	2.67×10^{-4}	1.30
Mean	1.38	6.04×10^{-4} a*	7.91×10^{-4} a*	1.37

* The least square difference at $P < 0.05$ according to Student-Newman-Keuls test = 9.88×10^{-4} .

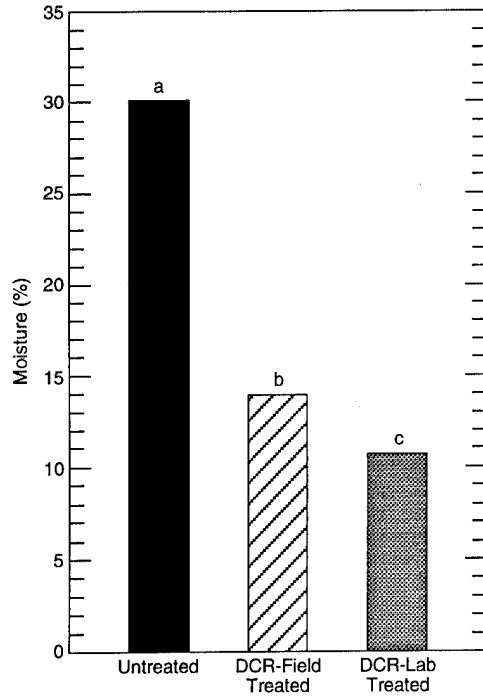


Figure 10. Changes in soil water content of untreated and DCR-treated material in the laboratory and field.

compacted clays increased significantly after freezing and thawing. Thermal cracking at low temperatures can further exacerbate the problem. Although in our single-cycle case the difference in hydraulic conductivity was not significant, the tendency was toward a greater conductivity, which agrees with the findings of Chamberlain.

Soil water content

The water content of untreated asphalt tar was around 30% by weight (Fig. 10). The water content of DCR-treated material treated in SOUND's on-site laboratory varied between 6.1 and 15.8%. The water content of field-treated material varied between 10.2 and 16.6%. The water content of untreated material was significantly greater than

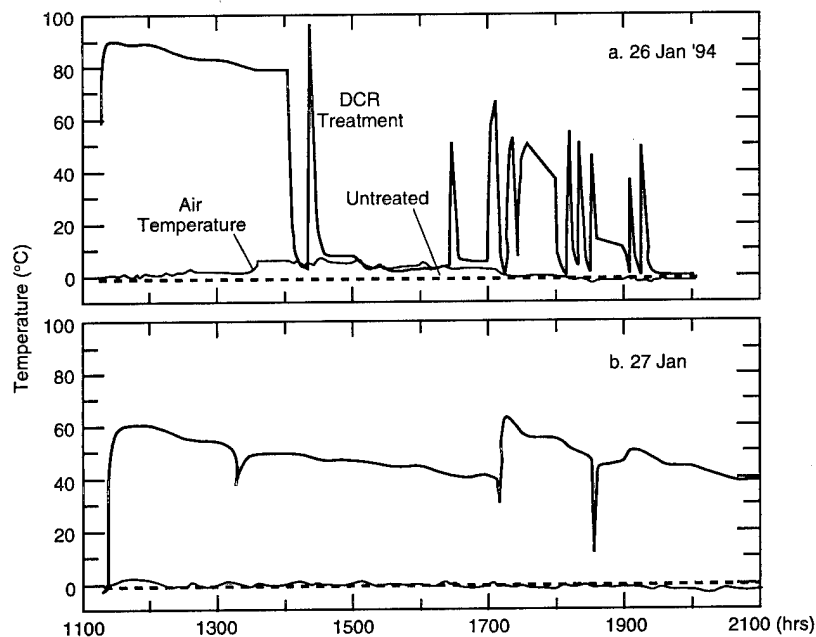


Figure 11. Changes in air, stockpiled untreated and DCR-treated material temperatures.

the DCR-treated material. This apparent dehydration in the treated material is partly caused by the formation of $\text{Ca}(\text{OH})_2$ and partly caused by the release of steam in the exothermic reaction (eq 1). The field-treated material contained significantly more water than the laboratory-treated material.

Soil temperature

Changes in the temperature at 2 m above the ground surface and in the untreated and DCR-treated materials are shown in Figure 11; 15 peaks of elevated temperatures were recorded for DCR-treated material. The temperature of the treated material increased to between 35 and 95°C, while untreated material remained close to 0°C on both sampling days. On 26 January, air temperatures started increasing after 1130 hours and reached a maximum of 6°C in an unshaded position.

Chemical analyses

Many of the volatile organics in soil were below the limits of detection (Carroll 1994). Statistically significant differences between untreated and DCR-treated soils were only found for acetone, 2-butanone, 4-methyl-2-pentanone and total xylenes (Table 6). With the exception of total xylenes, volatile organic concentrations were higher in the treated samples. In the TCLP extracts, treated samples had higher concentrations of 2-butanone, 2-hexanone, total xylenes and TPH (Table 7).

We can place these concentrations in perspective by examining Alaska or Federal drinking

water standards for specific constituents (Table 7). In all cases, drinking water standards are at least three orders of magnitude greater than the highest measured concentrations. Based on the specific analyses conducted in this work, neither the untreated nor the DCR-treated samples pose any significant environmental risk for drinking water.

Even though these soil and TCLP concentrations were low, where significant differences were found, they generally were higher in the treated material than in the untreated soil. This is contrary to what one might have expected. There are a number of possible explanations for this finding. The mixing process broke large, solid tar chunks into more finely dispersed material, thereby greatly increasing the surface area and reactivity of the tar to the extracting reagents. Other possible explanations include heating and oxidation of the tar during the mixing process. The DCR process is strongly exothermic, producing very high temperatures during and after the mixing (Fig. 11). It was also clear that initially the hydrophilic CaO and the tar did not mix properly because the tar was solid and the heat of mixing was insufficient to properly disperse the reagent into the tar. As mentioned previously, the final product still contained some fist-size tar balls.

Payne et al. (1994) discuss laboratory-scale applications of the DCR technology to three other contaminated soils from Shemya. Because these soils contained liquid wastes such as fuels, the DCR process generally lowered organic concentrations in the TCLP extracts. For example, ben-

Table 6. Total soil concentrations of specific organics and TPH (mean ± 1 s.e.). Statistically significant differences are designated by different lower-case letters.

Compound	Untreated ($\mu\text{g kg}^{-1}$)	Treated ($\mu\text{g kg}^{-1}$)
Acetone	66 \pm 14a	466 \pm 14b
2-Butanone	11 \pm 5a	266 \pm 12b
Benzene	0.0 \pm 0.0a	3.9 \pm 2.1a
4-Methyl-2-pentanone	0 \pm 0a	21 \pm 2b
Toluene	7.1 \pm 1.8a	4.8 \pm 1.6a
2-Hexanone	29 \pm 23a	48 \pm 13a
Ethylbenzene	6.7 \pm 1.4a	6.5 \pm 1.5a
Total Xylenes	64 \pm 13a	31 \pm 3b
TPH*	2602 \pm 621a	2160 \pm 254a

* mg kg^{-1} .

Table 7. TCLP extract concentrations of specific organics and TPH (mean ± 1 s.e.). Statistically significant differences are designated by different lower-case letters.

Compound	Untreated ($\mu\text{g L}^{-1}$)	Treated ($\mu\text{g L}^{-1}$)	Alaska or Federal std* ($\mu\text{g L}^{-1}$)
Acetone	23 \pm 14a	156 \pm 111a	na [†]
2-Butanone	1.0 \pm 0.6a	6.4 \pm 1.1b	200,000
Benzene	0.0 \pm 0.0a	0.0 \pm 0.0a	5
4-Methyl-2-pentanone	1.0 \pm 0.4a	2.0 \pm 0.5a	na
Toluene	0.14 \pm 0.14a	0.17 \pm 0.17a	1,000
2-Hexanone	0.0 \pm 0.0a	1.7 \pm 0.1b	na
Ethylbenzene	0.0 \pm 0.0a	0.39 \pm 0.25a	700
Total Xylenes	1.2 \pm 0.1a	2.4 \pm 0.4b	10,000
TPH	730 \pm 20a	1240 \pm 70b	na

* Payne et al. (1994)

† None applicable.

zene concentration from a fire training pit site was lowered from 110 $\mu\text{g L}^{-1}$ to nondetectable levels; this was significant because the regulatory limit for benzene in drinking water is 5.0 $\mu\text{g L}^{-1}$. Under appropriate conditions, the DCR process can significantly lower organic chemical concentrations.

CONCLUSIONS

The choice of solid asphalt tar to test the DCR technology in the field was unfortunate. The DCR process is designed to work with organics in the liquid phase. Preliminary laboratory studies both before and on Shemya indicated that laboratory-scale mixers at laboratory temperatures were adequate to heat the tar to the liquid state producing an acceptable product (Payne et al. 1994). The field scale trial was not as successful as there were still fist-size tar balls present in the product. Under cold field conditions, either heating of the tar prior to mixing or a more vigorous mixer might work to produce a better product.

The DCR technology had significant effects on the soil physical and chemical properties. The field demonstration led to a significant decrease in moisture and a significant increase in temperature during the mixing step, to a maximum of 95°C. The resultant product had a relatively low specific gravity (2.08 g cm^{-3}) and a coarse texture (37% gravel, 56% sand and 6% fines). Because of the coarse texture, the treated soils had high hydraulic conductivities ($> 2.7 \times 10^{-4} \text{ cm s}^{-1}$). Reduction of hydraulic conductivities to a regulatory limit of 1.0×10^{-5} for some applications will necessitate mixing with finer textured silts or clays.

There were a few significant differences in chemical concentrations between DCR-treated and untreated soil, with the DCR-treated material generally having higher concentrations. This counterintuitive outcome is probably attributable to a poor mixing of the lime reagent and asphalt tar and to the greater surface area of the treated end product. However, in all cases, contaminant levels in TCLP extracts were well below drinking water standards. In an independent laboratory-scale test on fuel-contaminated soils from Shemya, the DCR process successfully lowered organic chemical concentrations.

The DCR technology converted a chunky tar material into a more finely dispersed soil-like material, which should facilitate its beneficial reuse as a landfill liner or road sub-base.

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